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1. REPORT DATE (DD-MM-YYYY) 26-03-2014		2. REPORT TYPE Final Report		3. DATES COVERED (From - To) 15-Dec-2011 - 14-Apr-2013	
4. TITLE AND SUBTITLE Hydrogen Photo-production from Ethanol and Water over Au/TiO2 Rutile Single Crystal				5a. CONTRACT NUMBER W911NF-12-1-0024	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 611102	
6. AUTHORS Russell F Howe, Hicham Idriss				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Aberdeen Aberdeen Centre for Energy Regulation and Obesity (/				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 58534-CH-II.1	
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT This project in its final form has focused on hydrogen production from ethanol and water-ethanol mixtures over a range of different gold-titania photocatalysts. Gold supported on a commercial anatase: rutile mixture has been found to be 3 times more active for hydrogen production than the previously reported gold on anatase photocatalysts. Other products detected were ethene and acetaldehyde; these products were enhanced in the presence of water. In-situ EPR spectroscopy was used to show that the gold nanoparticles act as sinks for electrons produced in the conduction band of the titania. Experiments with gold supported on Degussa showed that this					
15. SUBJECT TERMS Photocatalysis hydrogen ethanol gold titania					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			Russell Howe
					19b. TELEPHONE NUMBER +44-012-2427

## Report Title

Hydrogen Photo-production from Ethanol and Water over Au/TiO<sub>2</sub> Rutile Single Crystal

### ABSTRACT

This project in its final form has focused on hydrogen production from ethanol and water-ethanol mixtures over a range of different gold-titania photocatalysts. Gold supported on a commercial anatase: rutile mixture has been found to be 3 times more active for hydrogen production than the previously reported gold on anatase photocatalysts. Other products detected were ethene and acetaldehyde; these products were enhanced in the presence of water. In-situ EPR spectroscopy was used to show that the gold nanoparticles act as sinks for electrons produced in the conduction band of the titania. Experiments with gold supported on Brookite showed that this support was comparable in activity with anatase, although a Brookite: anatase mixed phase support gave higher activity than either pure Brookite or pure anatase.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

**Number of Papers published in peer-reviewed journals:**

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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### (c) Presentations

C.A.Main, K.A.Connelly, R.F Howe, "Photocatalytic Hydrogen Production from Ethanol over Gold-Titania (P25 and Brookite)", student poster presented by Callum Main, Fourth International Conference on Semiconductor Photochemistry, Prague, Czech Republic, June 2013.

Number of Presentations: 1.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Callum Main	1.00	
<b>FTE Equivalent:</b>	<b>1.00</b>	
<b>Total Number:</b>	<b>1</b>	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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### Names of Personnel receiving masters degrees

NAME

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**Total Number:**

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### Sub Contractors (DD882)

### Inventions (DD882)

### Scientific Progress

See attachment

### Technology Transfer

## **ARO Proposal 58534-CH-II**

### **Foreword**

The Final Report presented here addresses the modified Work Plan approved in December 2011. The major component of the revised budget was a 12 month stipend for an MSc student. This student (Callum Main) was recruited and began his project in May 2012, completing all experimental work by June 2013. His thesis has not so far been submitted. A PhD student (Karen Connelly) who was supported by the University of Aberdeen also undertook experimental work on the project in this period, using facilities and consumables funded by the grant. (Her PhD examination was completed successfully in March 2014). The following report summarises work undertaken by both students.

### **Statement of Problem**

This project is concerned with the photocatalytic production of hydrogen from ethanol over gold-titania photocatalysts. The project builds on an earlier study in Aberdeen [1] showing that hydrogen production rates of up to 2 litres of hydrogen per kg of catalyst per minute could be achieved by UV – irradiation of gold-anatase photocatalysts in ethanol. The challenges faced were (a) understanding how this reaction works and (b) improving the performance of the photocatalysts to enhance the hydrogen production rates. The original proposal was to carry out surface science experiments with single gold clusters deposited on rutile single crystals, in parallel with slurry phase photocatalytic measurements on powdered catalysts. The departure of one of the PI's on the project (Professor Hicham Idriss) from Aberdeen has caused the work plan to be further modified to focus exclusively on powdered catalysts (Part 2 of the modified work plan approved in December 2011). The project has looked at the improvements in hydrogen production achieved by supporting gold nanoclusters on anatase: rutile composite supports compared with gold on anatase alone. The importance of phase boundaries in the support has been confirmed by showing that gold supported on brookite: anatase composite supports is also more active for hydrogen production than gold on anatase or brookite alone. Electron paramagnetic resonance studies of the gold: anatase-rutile catalysts have provided new information about reaction pathways and the origins of ethylene, which is a major gas phase reaction product along with hydrogen when ethanol: water mixtures are reacted.

### **Summary of Results**

#### **Gold: anatase-rutile catalysts: characterisation**

Gold nanoclusters were supported on Evonik P25, a commercially available form of titania which is a 70:30 anatase: rutile mixture, at loadings up to 8 wt % gold. High resolution TEM images showed that the titania support comprises a close intergrowth of anatase and rutile crystallites, while the gold nanoclusters have a spherical morphology and are associated with both anatase and rutile components. (Figure 1). The particle size distributions of the gold clusters were found to be closely similar for all gold loadings studied (Table 1), and high resolution XPS analysis indicated the gold to be zerovalent.

Similar characterisation was undertaken on the same catalysts after they had been used in the ethanol to hydrogen reaction. There was no change in mean gold particle sizes within the standard deviations of the statistical analysis following photocatalytic reaction in ethanol or water-ethanol mixtures.

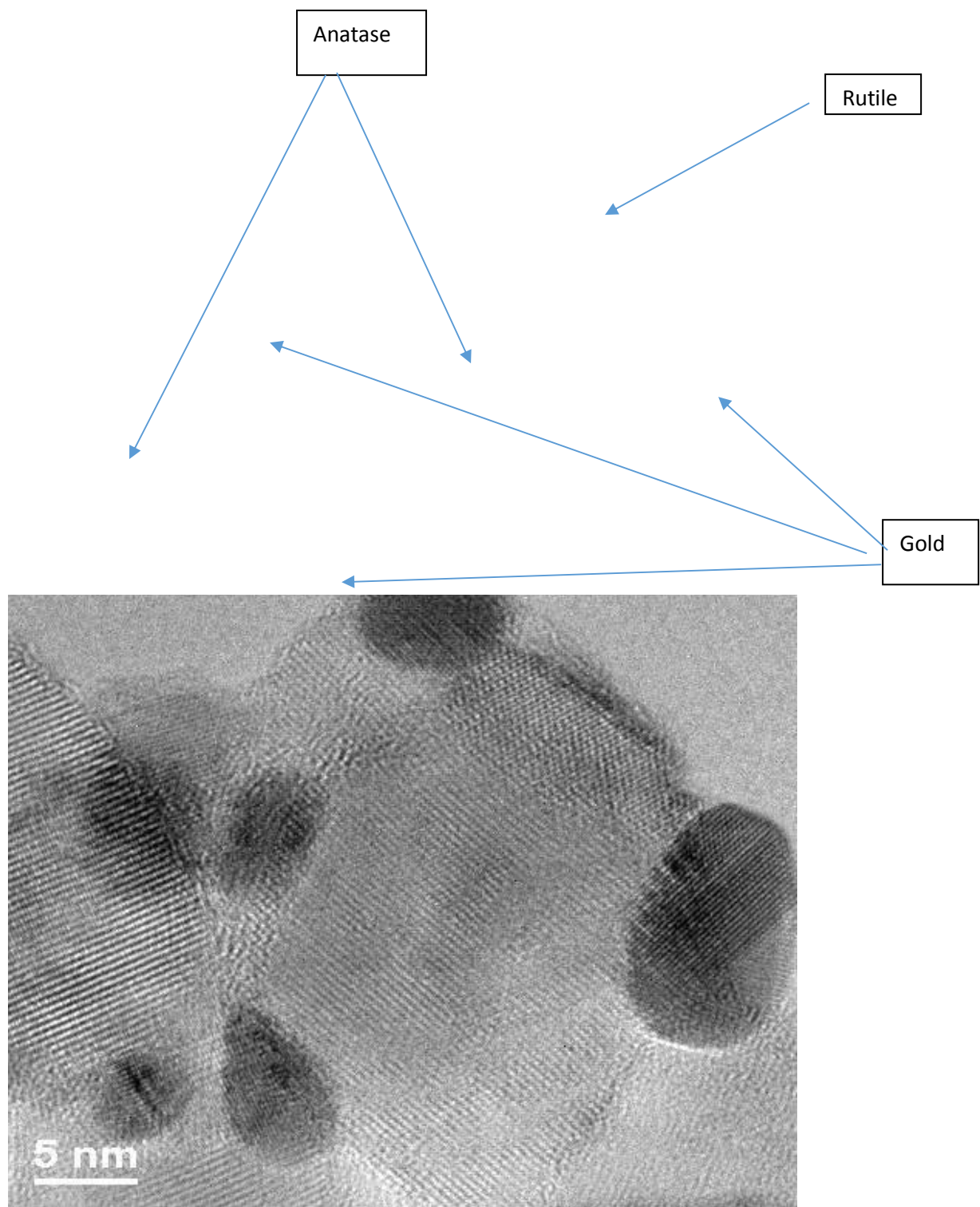


Figure 1: High resolution TEM image of 8% Au on P25, showing gold nanoparticles, and intergrowth of anatase and rutile phases of titania

Au Wt. % on P25	No. of Au nanoparticles	Nanoparticle diameter range (nm)	Mean	St. Dev.
1.5	88	1 - 8	3.8	2.0
4	242	1 - 10	4.6	2.4
6	230	1 - 9	4.4	1.9
8	360	1 - 8	3.9	1.6

Table 1: Statistical analysis of gold particle size distributions on P25, determined by high resolution TEM

### Gold: P25 catalysts: catalyst evaluation.

Catalytic reactions were conducted in a liquid slurry reactor under a N<sub>2</sub> atmosphere. The catalyst load was varied to ensure a linear production rate under UV illumination; optimum loading was 10 mg for a 100 mL reactor containing 20 mL of ethanol or water: ethanol mixture. Catalysts were typically prereduced overnight in hydrogen at 673 K and 1 bar pressure. UV light was provided by a concentric set of 6 15 watt UV lamps surrounding the reactor at a distance of 5 cm. The measured light flux from each lamp was ca. 1.5 mW cm<sup>-2</sup>. Gas phase product analysis was conducted using 2 gas chromatographs fitted with thermal conductivity detectors or by using infrared spectroscopy with a 10 cm gas cell.

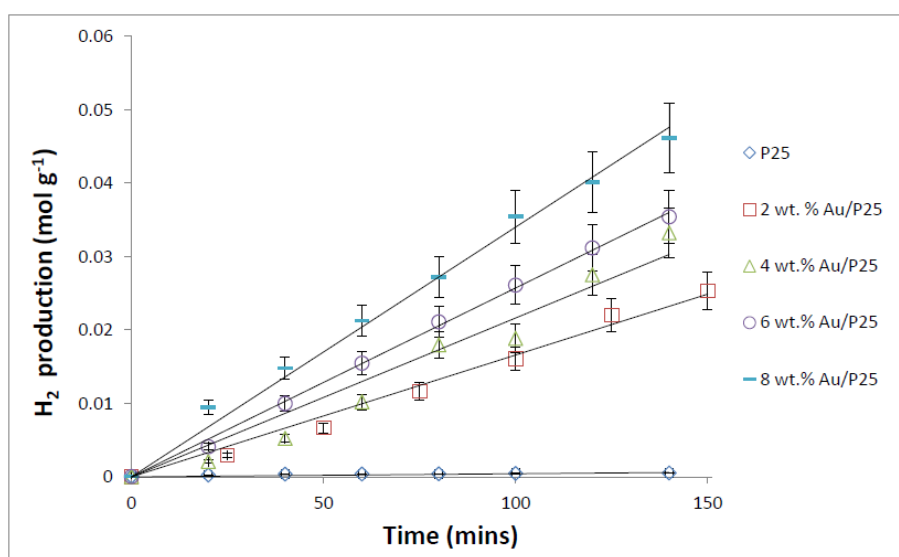


Figure 2 : Photocatalytic hydrogen production from ethanol over various Au/P25 catalysts

Figure 2 shows typical hydrogen production curves for gold:anatase-rutile catalysts containing different loadings of gold. The P25 support alone was virtually inactive for this reaction, while the rate of hydrogen production increased with increasing gold loading on the titania. The highest rates of  $\sim 3 \times 10^{-4}$  mol g<sup>-1</sup> min<sup>-1</sup> should be compared with  $\sim 1 \times 10^{-4}$  mol g<sup>-1</sup> min<sup>-1</sup> reported previously [1] for gold supported on anatase. Gold supported on rutile was reported previously to show a hydrogen production rate 2 orders of magnitude less than gold on anatase [1]. The figures obtained here for gold on the commercial 70:30 anatase:rutile mix clearly indicates that there is a strong synergistic effect from having both phases present in the support.



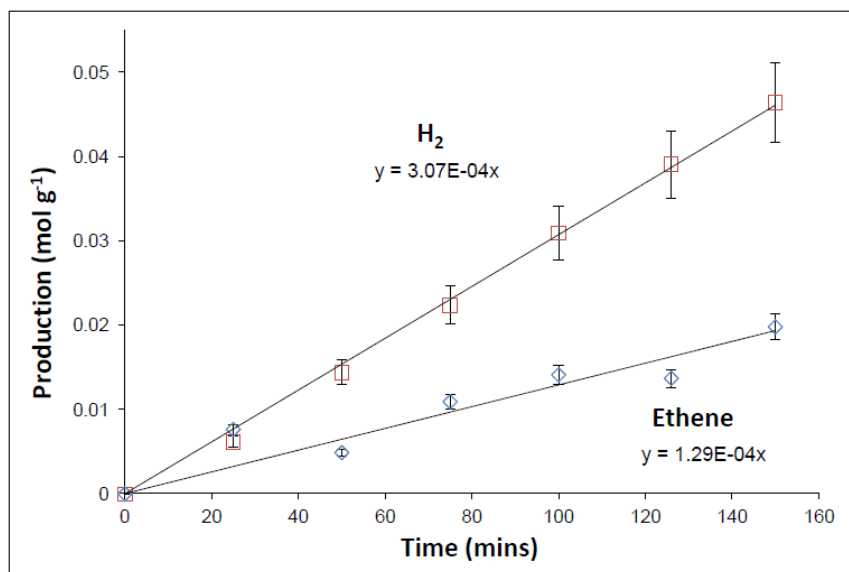


Figure 3 Comparison of the rate of production of hydrogen and ethylene from ethanol over 8% gold on P25.

The other major gas phase product detected by both GC and infrared analysis was ethylene (ethene). Figure 3 shows typical hydrogen and ethylene production over an 8% gold on P25 titania catalyst during UV irradiation of ethanol. The ethylene production rate in this example is about 40% of the hydrogen production rate. The relative rates of production of hydrogen and ethylene were found to depend markedly on the presence of water in the ethanol, as shown in Figure 4.

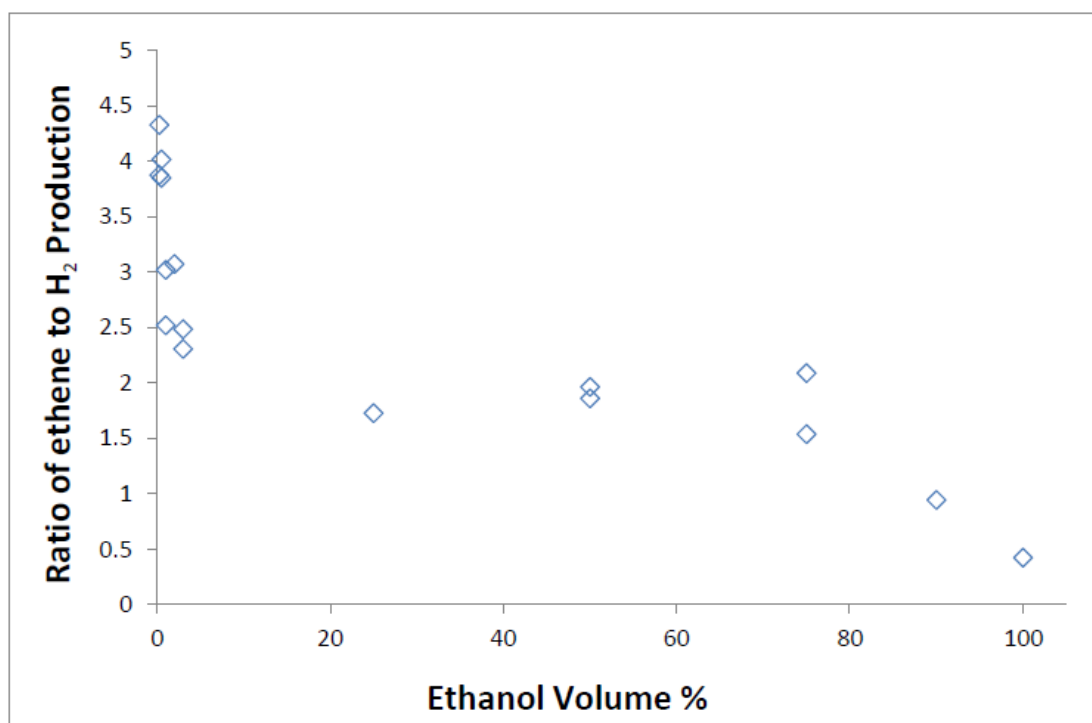


Figure 4. Comparison of rates of ethylene and hydrogen production from ethanol: water mixtures over 8% gold on P25 catalyst .

The rate of ethylene production exceeds that of hydrogen once the water content exceeds 10 volume %, and at very low ethanol concentrations ethylene is the major product.

### Gold:brookite catalysts: catalyst evaluation

Brookite is a titania phase which has received much less attention than anatase or rutile as a catalyst support. In this study, two 8 % gold: brookite catalysts were prepared using the same deposition-precipitation method used for the gold:P25 catalysts described above. One of these was on brookite which was 100 % phase pure (as estimated by X-ray powder diffraction) while the other was on an anatase:brookite mixture (~80% brookite). Figure 5 compares hydrogen production from these different catalysts with those of 8 % gold on P25 (from 100 % ethanol).

The rate of hydrogen production from 8 % gold:brookite ( $1 \times 10^{-4} \text{ mol g}^{-1} \text{ min}^{-1}$ ) is similar to that reported previously [1] for gold: anatase. The 8 % gold: brookite-anatase mixture shows a 50% higher rate, supporting the conclusion from the gold:P25 experiments that the presence of mixed phases enhances the catalyst performance for this reaction. It can be seen from the Figure however that the gold: brookite-anatase catalyst does not achieve the hydrogen production rate achieved with gold:P25. The Figure also shows that the brookite supports in the absence of gold have negligible activity for hydrogen production.

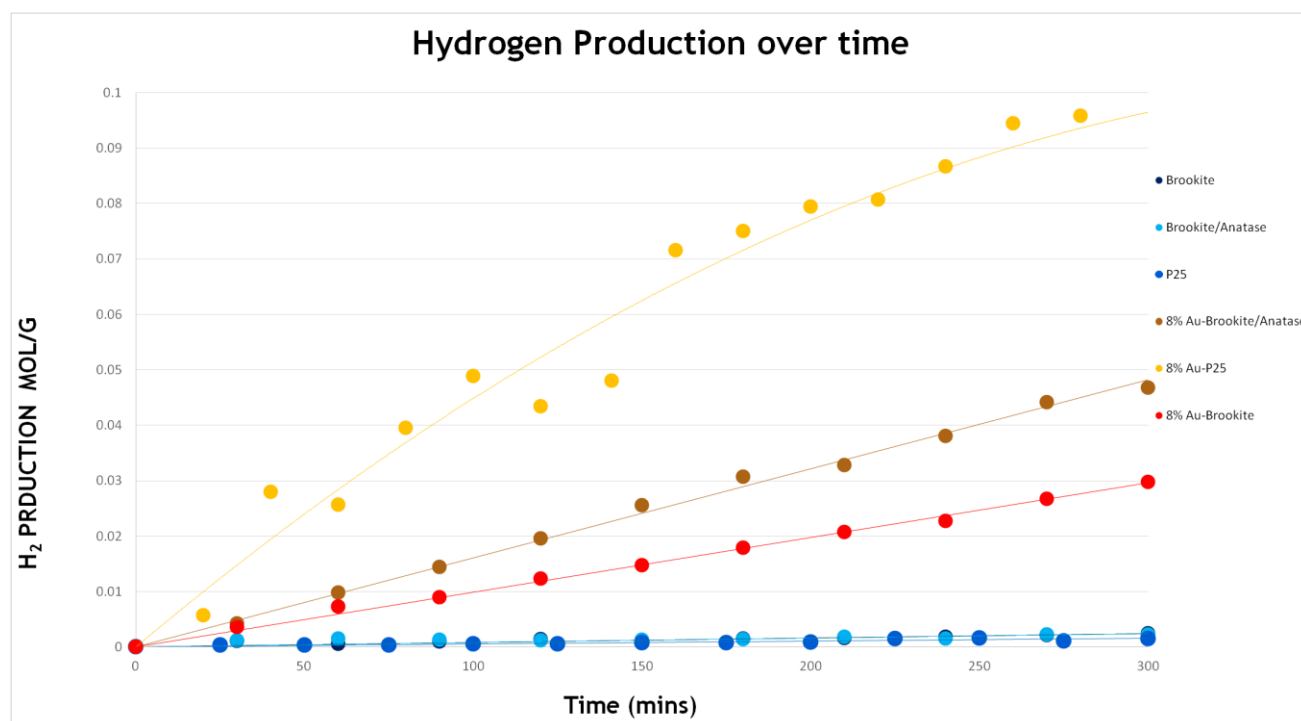


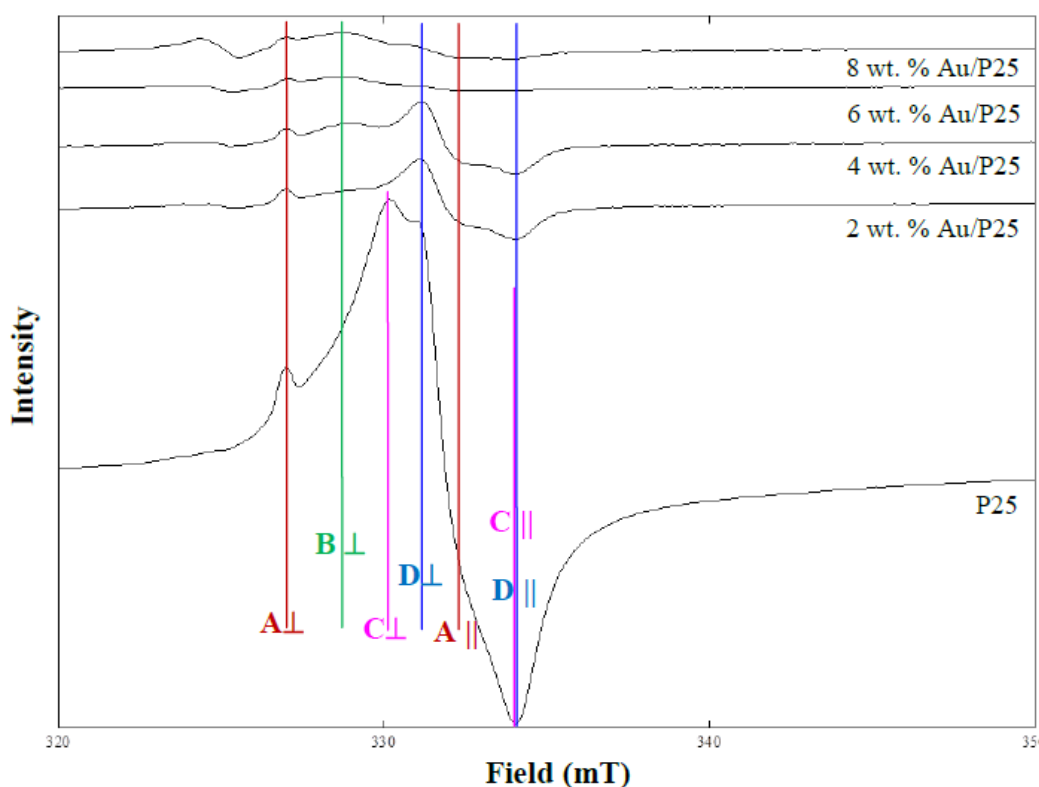
Figure 5: Comparison of hydrogen production from 100 % ethanol over different catalysts

### Gold: P25 catalysts: EPR studies

EPR spectroscopy has been used to investigate the trapping of electrons in P25, the influence of gold nanoclusters on these electron trapping events, and the effects of ethanol. The experiment is conducted by irradiating samples held in vacuum cells mounted in the sample cavity of the EPR spectrometer with filtered light (320-900 nm) from a xenon arc lamp.

When P25 alone is irradiated in vacuo at 80 K, strong signals of  $\text{Ti}^{3+}$  appear only after irradiation is stopped. (Figure 6) These signals are due to electrons promoted into the conduction band of the semiconductor during irradiation which become trapped when irradiation is stopped. [2] At least 4 different signals are present (labelled A, B, C and D in Figure 6). These are known [3] to be due to surface and bulk trap states in anatase and rutile. The most dominant signals are those of electrons trapped in the rutile phase, consistent with earlier conclusions that the trap states in rutile are deeper than those in anatase [2].

The addition of gold to the P25 suppresses the electron trapping behaviour when the gold:P25 photocatalysts are irradiated in vacuo. This can be seen clearly in Figure 6, which compares the EPR spectra measured in each case following irradiation. The number of electrons trapped in the titania decreases as the gold loading is increased, which is completely consistent with the concept of electron transfer to the gold nanoparticles [1].



**Figure 6:** EPR spectra of gold:P25 photocatalysts measured at 80 K following irradiation in vacuo at 80 K. Marked are the perpendicular and (where resolved) parallel components of 4 different  $\text{Ti}^{3+}$  signals.

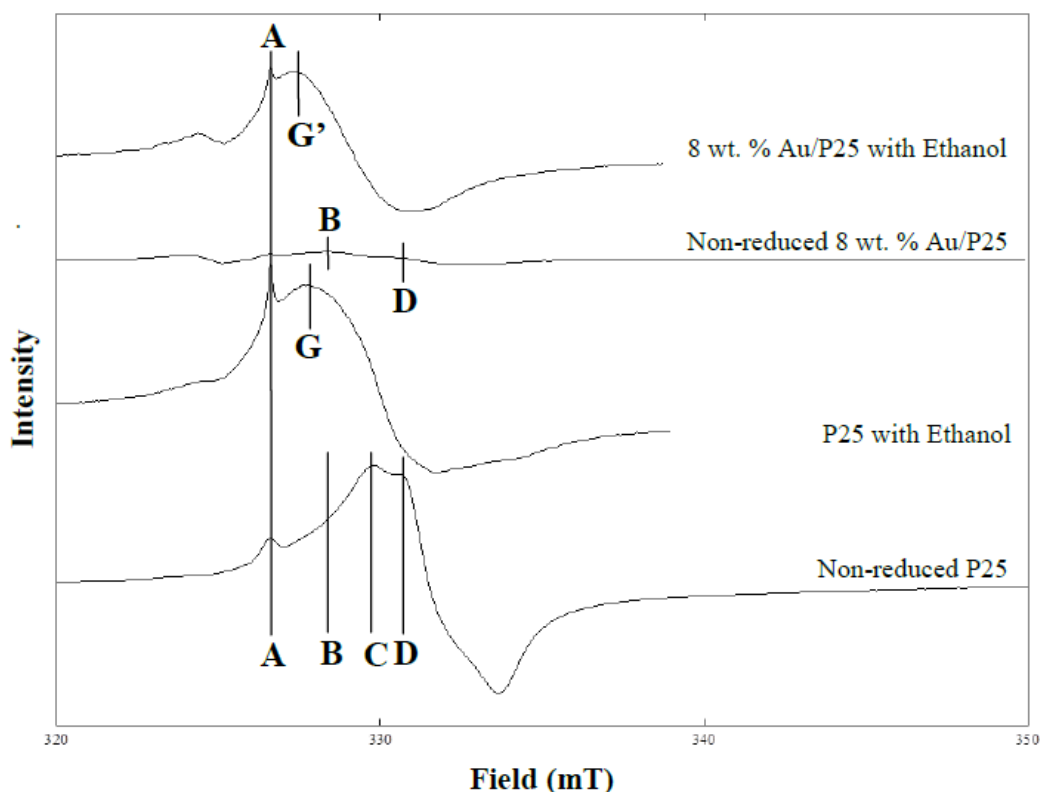
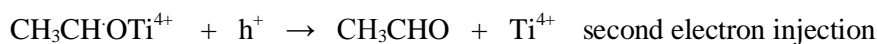


Figure 7: Comparison of EPR signals measured from P25 and 8 % gold:P25 following irradiation in vacuo and in the presence of ethanol at 80 K.

When the catalysts are irradiated in the presence of ethanol, the behaviour observed is completely different. (Figure 7). Trapped electron signals are observed during irradiation which persist when irradiation is stopped, and the number of trapped electrons seen with 8% gold: P25 is only slightly less than P25 alone. Furthermore, the EPR signals of the trapped electrons in this case are quite different from those formed after irradiation in vacuo. Further work is needed on this, but the initial interpretation is that adsorbed ethanol stabilises surface trap states so that photo-produced electrons remain in them at 80 K, even in the presence of gold.

A further important observation at 80 K is that no signals of organic radicals were detected during in-situ irradiation in the presence of ethanol. The mechanism proposed for production of hydrogen from ethanol involves two one electron transfers from ethanol to the titania [1]:



The absence of any detectable signal from the proposed  $\text{CH}_3\text{CH}^+\text{OTi}^{4+}$  radical intermediate at 80 K means that either this species is too short lived at this temperature to be detected, even under steady state continuous irradiation, or that in fact the electron transfer is a concerted two electron process. Experiments at lower temperature (4 K) will be necessary to determine the correct explanation.

A further mechanistic question raised by this work is the origin of the ethylene product. The above mechanism implies formation of one mole of acetaldehyde for each mole of hydrogen produced ( and very recent work by Corma et al. [4] with very low loadings of gold on anatase have shown that this is approximately the case). In the work presented in this report analysis of the gas phase by infrared spectroscopy revealed the presence of acetaldehyde, but accurate quantification was not possible.

Ethylene production appears however to occur via a separate mechanism (Figure 4) and is enhanced by the presence of water. A possible mechanism involves hydroxyl radicals generated by attack of valence band holes on adsorbed water molecules (in competition with the reactions shown above with adsorbed ethanol). There is indirect evidence for hydroxyl radical generation on irradiation of titania in the presence of liquid water [5], and attack of hydroxyl radicals on ethanol to generate ethylene is a known homogeneous reaction [6]. No hydroxyl radicals were detected in this work at 80 K, but measurements at 4 K are needed to confirm or refute this suggestion.

## Summary

The work conducted here has in the first place confirmed other reports[7] that gold supported on P25 titania is more active for photocatalytic hydrogen production from ethanol than gold on anatase or rutile. The importance of phase boundaries in the titania support in enhancing hole: electron separation and hence photocatalytic activity known for P25 was also found to occur to a lesser extent with a brookite:anatase mixture. This work has shown for the first time that ethylene can be a major product of the ethanol photocatalytic reaction in the presence of water, at least with high gold loadings (with a corresponding reduction in the desired selectivity of ethanol conversion to hydrogen). Finally, EPR spectroscopy has been used for the first time to observe the fate of the conduction band electrons produced on irradiation of these catalysts, both in the presence and absence of ethanol.

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